Modelling of adsorption on atmospheric solid particles

PhD Thesis Summary

György Hantal

Supervisors:
Dr Pál Jedlovszky, DSc
and
Dr Sylvain Picaud, PhD

Chemistry Doctoral School (Head: Prof. György Inzelt), Theoretical and Physical Chemistry, Structural Chemistry Doctoral Programme (Head: Prof. Péter Surján)

Institute of Chemistry, Eötvös Loránd University
Faculty of Science

Louis Pasteur Doctoral School (Head: Prof. Mironel Enescu)

Institute UTINAM, University of Franche-Comté
Faculty of Science

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1 Introduction and the goals of the thesis

During the last decades growing attention has been paid to atmospheric chemistry. This considerably young discipline is basically based on experimental methods. Atmospheric processes, however, are difficult to study experimentally. Our possibilities are quite limited because the experiments should be performed under *controlled* atmospheric conditions and the measurement of different chemical species should be carried out at the same time. Theoretical methods and particularly simulation techniques can complement and support our experimental understanding. Numerical methods have already been used successfully in numerous cases to reduce extremely complicated reaction mechanisms by finding the key processes and species. Theoretical methods enable us to create models by identifying the major features and elements of the process studied. Successful predictions made by the model can support its validity.

With computer simulation techniques one can go farther because it is possible to make experiments on the theoretical model that can reveal a lot of details that are hidden from the experimentalists. Atomistic simulations allow one to observe the microscopic details of the process studied and, which is at least as much or more important, make it possible to compute ensemble averages on the model system without any approximation.

In my work, I used theoretical methods to study phenomena related to two of the most abundant atmospheric solid particles, namely ice and soot. A microscopic approach is desirable to the profound understanding of the effects of these two kinds of solid particle. My research was dedicated to three main topics in connection with soot and ice.

The first topic concerns the adsorption of three different volatile organic compounds (VOCs), such as acetone, formic acid and benzaldehyde on the ice surface. The VOC molecules are released into the atmosphere mainly from anthropogenic sources, and are suspected to have a significant role in the chemistry of the atmosphere either through the products of their photo degradation, or by the production of contaminant and harmful tropospheric ozone.

My second research topic concentrates on the water uptake at the soot surface. Soot particles emitted in particular by aircrafts have an undeniable role in the nucleation of ice particles in the oversaturated atmosphere. However, the mechanism of the nucleation and the key factors in this procedure are not known.

My third subject deals with the chemical activity of soot particles. I investigate how the soot surface influences the oxidation of polycyclic aromatic hydrocarbons (PAHs) by the OH radical which is the most abundant oxidising agent in the atmosphere.

2 Results

The most relevant results presented in the thesis can be summarised as follows.

2.1 Adsorption of acetone, formic acid and benzaldehyde on ice

1. The adsorption of the three adsorbate molecules can be characterised by the Langmuir isotherm at only low pressure where the admolecules are far enough from each other and, thus, their adsorption takes place independently from each other. At higher pressure, the adsorption isotherms deviate from what the Langmuir or the BET isotherm predict on the basis of the adjustment of the low range part of the isotherms.

2. At higher surface coverage both the Langmuir and the BET theory fail because the lateral interactions are not negligible between the adsorbates. Moreover, the adsorption sites are not equivalent to each other either because the orientational preferences change by increasing pressure, thus the admolecules are not bound to the surface in the same way.

3. The monotonous rising of the $\Gamma(p_{rel})$ isotherms suggests that multilayer adsorption occurs in the case of all of the three adsorbates.

Adsorption of acetone on ice

4. During the adsorption of the acetone molecules, the monolayer of the admolecules does not exhibit a particular stability.

5. The bivariate orientational maps of the adsorbed acetones show that at low pressure, a flat orientation is preferred in which the formation of two hydrogen bonds between water hydrogens and a carbonyl O of an acetone is possible. This finding is confirmed by the interaction energy distributions. Increasing pressure leads to the appearance of a second orientation in which the acetone

molecules can maintain only one hydrogen bond with the surface. In this orientation the plane of the molecule is perpendicular to the ice surface enabling thus them to maximise their number at the surface. In systems where molecules belonging to the second layer can also be found, a third alignment can be identified corresponding to acetones oriented away from the surface by their carbonyl group. Molecules of the second layer can stabilise this molecular orientation.

6. The agreement between the obtained results and the experimental ones is very good. The measured heat of adsorption is excellently reproduced by the simulation ((-51.4 ± 1.3) kJ mol^{-1}), but the comparison of the simulated adsorption isotherm to measured curves is not obvious because of the diversity of experimental data. However, the deviation of the obtained $\Gamma(p_{rel})$ isotherm from the experimental data sets remains in the same order as the reported deviation of the various experimental isotherms from each other.

Adsorption of formic acid on ice

7. The saturated monolayer of the formic acid molecules proves to be considerably stable.

8. At low surface coverage a perpendicular alignment of the formic acid molecules is preferred. In this orientation the formic acid molecule can form two exceptionally strong hydrogen bonds with the surface. At higher pressures a second and a third orientation (both perpendicular to the surface) become also preferred. In these orientations the formation of only one hydrogen bond is possible with the ice but a molecule of these types can form either two O-H$\cdots$O type hydrogen bonds with another admolecule in the same layer or an O-H$\cdots$O and a C-H$\cdots$O type hydrogen bond with a formic acid molecule belonging to the next layer. The presence of these hydrogen bonding motives leads to the fact that all formic acid molecules can participate in a hydrogen-bonding network formed through the adsorption layers. In the outmost layer, the admolecules may lie parallel to the surface and form hydrogen bonds with those of the previous layer.

9. The comparison between the simulations and the experimental measurements carried out jointly with our study shows that simulated properties are in good agreement with the ones measured at a temperature 20 K higher than that

of the simulations. This shift probably originates from, on one hand, the uncertainty of the determination of the μ_0 value (i.e. where the condensation occurs) in the simulations, and, on the other hand, that of the Antoine parameters used to extrapolate the p_0 value.

Adsorption of benzaldehyde on ice

10. The monolayer of the adsorbed benzaldehyde molecules exhibits high stability in a large pressure range.

11. Three main orientations are identified at the ice surface. In the first, lying orientation, the formation of a hydrogen bond between the adsorbates and water molecules is possible. Furthermore, the enhanced electronic density of the benzene ring may also interact with the highly electronegative water O atom. In the second orientation, benzaldehyde molecules are perpendicular to the surface, and they can maintain only one hydrogen bond with the ice phase. In the third orientation, the carbonyl group is oriented toward the gas phase. The appearance of this orientation necessitates the presence of molecules in the next layer.

12. The adsorption isotherm as well as the obtained heat of adsorption ((-59.4 $\pm$ 5.1) kJ mol^{-1}) are in excellent agreement with the experience ((-61.4 $\pm$ 9.7) kJ mol^{-1}) performed jointly with our study.

2.2 Adsorption of water on soot

13. Our model soot particles are more realistic from a chemical point of view than those used in previous studies because the structure of our particles are relaxed by the reactive AIREBO potential after the creation of holes modifying thus the porosity of the particles.

14. The first adsorbed water molecules are located at positions where the wall of the cavity is locally of rather large curvature.

15. The main driving force of the adsorption is the possibility of forming a hydrogen bond between a water molecule already incorporated inside the cavity and a newly adsorbed one. Thus the adsorption of the first molecule is of high importance. The appearance of the first adsorbed molecules can be shifted

toward lower pressures by placing a COOH group inside the cavity: The adsorption capacity is not affected by the presence of one COOH group but the cavity becomes filled at much lower pressure.

16. The morphology of the cavity influences the efficiency of the water adsorption: the more spherical a pore is the more efficiently it can be filled.

2.3 Reactivity of soot particles

17. A new model has been presented to characterise the influence of a soot particle on the oxidation reaction of polycyclic aromatic hydrocarbons (PAHs) by the OH radical. The characterisation is carried out by comparing the reaction rate of the oxidation reaction that takes place in the gas phase to that occurring when the PAH molecules are adsorbed on soot. In the model, the soot–PAH and PAH–OH interactions are calculated in terms of the semi-empirical-dispersion (SE-D) model which allows for the description of the dispersion interaction in a very simple and efficient way.

18. The kinetics of the oxidation reaction is described in terms of the TST model.

19. The physisorption of PAH molecules affects neither the internal vibrational motions nor the electronic ones. The rotation as well as the translation in a plane parallel to the surface remain unchanged but the motions perpendicular to the soot become hindered and are thus treated as vibrational motions.

20. Translational, rotational and vibrational motions are described by analytical expression within the rigid rotor and harmonic oscillator approximations.

21. It turned out that the primary inhibiting effect of the soot surface (namely that it hides one side of the PAH molecule from the OH attack) is compensated by the energy gain of the transition state of the reaction. The joint quenching of this two effects results in similar reaction rates of the oxidation of PAHs by OH in the gas phase and when the PAH molecule is adsorbed on a perfect carbonaceous surface.

3 Papers published in the subject of the thesis

1. Adsorption Isotherm of Formic Acid on the Surface of Ice, as Seen from Experiments and Grand Canonical Monte Carlo Simulation.

P Jedlovszky, G Hantal, K Neurohr, S Picaud, P N M Hoang, P von Hessberg, J N Crowley
J. Phys. Chem. C **112**, 8976 (2008).

2. Investigation of the adsorption behaviour of acetone at the surface of ice. A grand canonical Monte Carlo simulation study.
G Hantal, P Jedlovszky, P N M Hoang, S Picaud
Phys. Chem. Chem. Phys. **10**, 6369 (2008).

3. A new semi-empirical model for the oxidation of PAHs physisorbed on soot. I. Application to the reaction C6H6 + OH.
G Hantal, S Picaud, B Collignon, P N M Hoang, M T Rayez, J C Rayez
Mol. Sim. **35**, 1130 (2009).

4. Molecular-scale modeling of the adsorption of partially oxidized organic compounds on ice.
G Hantal, P Jedlovszky, L B Pártay, S Picaud, P N M Hoang
Trends in Phys. Chem. **13**, 1 (2008).

5. Adsorption of Benzaldehyde at the Surface of Ice, Studied by Experimental Method and Computer Simulation.
M Petitjean, G Hantal, C Chauvin, Ph Mirabel, S Le Calvé, P N M Hoang, S Picaud, P Jedlovszky
Langmuir published online, DOI: 10.1021/1a100169h.

6. Water adsorption isotherms on porous onion-like carbonaceous particles. Simulations with the grand canonical Monte Carlo method.
G Hantal, S Picaud, P N M Hoang, V P Voloshin, N M Medvedev, P Jedlovszky
submitted to J. Chem. Phys.

Papers published during the PhD, but not included in the thesis

7. A new method for determining the interfacial molecules and characterizing the surface roughness in computer simulations. Application to the liquid-vapor interface of water.
L B Pártay, G Hantal, P Jedlovszky, Á Vincze, G Horvai
J. Comp. Chem. **29**, 945 (2008).

8. Nuclear quantum effects in electronically adiabatic quantum time correlation functions: Application to the absorption spectrum of a hydrated electron.
   L Turi, G Hantal, P J Rossky, D Borgis
   J. Chem. Phys. **131** 024119 (2009).

9. Molecular Level Properties of the Water-Dichloromethane Liquid/Liquid Interface, as Seen from Molecular Dynamics Simulation and Identification of Truly Interfacial Molecules Analysis.
   G Hantal, P Terleczky, G Horvai, L Nyulaszi and P Jedlovszky
   J. Phys. Chem. C **113** 19263 (2009).

10. Molecular Level Properties of the Water Surface at the Interface with Various Fluid Phases, as Seen from ITIM Analysis of Computer Simulation Results.
    G Hantal, M Darvas, L B Pártay, G Horvai, P Jedlovszky
    J. Phys.: Cond. Matt. **in press**